It is clear that the position of the aquo complex at the extreme lower end of the observed spectrochemical series[4] is not due to a weak interaction between the coordinated water molecule and the copper(II) ion. The bond to the water molecule in the apical position is, in fact, quite strong, and the combined effect of the apical displacement of the metal ion and the strong apical bond must be to compress the energy separation between the $d_{x^2-y^2}$ and the d_{z^2} metal orbitals. Addison and Wicholas[4] predicted that this would be the case and also predicted that in a series of complexes $[Cu(cyclops)L]^+$ and [Cu(cyclops)X], where X^- and L are a variety of apically bound ligands, a wide range of metal atom apical displacements would be seen, with the displacement becoming greater for ligands higher in their observed spectrochemical series.

The two structures presently available in this series, that of **1** and that of [Cu(cyclops)NCO],[1] confirm this second prediction also. The out-of-plane displacement in **1** is only 0.32 Å, whereas in the cyanato-*N* adduct the corresponding value was 0.58 Å and the bond to the apical ligand was found to be exceptionally strong. Since these two compounds represent the extreme ends of the spectrochemical series seen, other macrocyclic cyclops complexes should exhibit apical metal atom displacements and apical bond strengths intermediate in value. It will be of interest to investigate the structures of such complexes and to seek to confirm the final prediction made by Addison and Wicholas that anionic apical ligands in this system should be found to interact much more strongly with the copper(II) ions than would normally be expected. The fact that the iodo ligand lies higher in the observed spectrochemical series than does water certainly seems to support this view, and we expect to see a very strong interaction with the iodo ligand in our forthcoming study of the structure of [Cu(cyclops)I].

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Registry No. **1**, 70178-69-7; **2**, 70178-67-5.

Supplementary Material Available: Table IX, calculated atomic fractional coordinates for hydrogen atoms of $[Cu(PreH)H_2O](ClO_4)\cdot H_2O$; Table X, calculated fractional atomic coordinates for hydrogen atoms of $[Cu(cyclops)H_2O](ClO_4)$; Table XI, a listing of structure factor amplitudes (×10) for $[Cu(PreH)H_2O](ClO_4)\cdot H_2O$; Table XII, a listing of structure factor amplitudes (×10) for $[Cu(cyclops)H_2O](ClO_4)$ (38 pages). Ordering information is given on any current masthead page.

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Crystal Structure of (Benzotriazolato)thallium(I) and Its Relation with the Mechanism of Corrosion Inhibition by Benzotriazole

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The crystal and molecular structure of (benzotriazolato)thallium(I) is described. The structure has been determined by using three-dimensional X-ray diffraction data collected by counter methods. Crystal symmetry is consistent with the monoclinic space group *C*2/*c*. The unit cell parameters are a = 26.605 (3) Å, b = 4.057 (1) Å, c = 12.173 (2) Å, β = 93.74 (1)°, and Z = 8; d_{calcd} = 3.268 g/cm^3 and μ(Mo Kα) 246.8 cm^{-1}. The structure was solved by Patterson and subsequent Fourier techniques. Full-matrix least-squares refinement converged to R_F = 0.022 and R_{wF} = 0.024 for 1297 reflections. The structure consists of sheets of Tl(I) ions separated by benzotriazole anions. Each Tl ion is coordinated by three N atoms of the ligand at distances of 2.725–2.792 Å and by three neighboring N atoms at 3.271–3.326 Å in a distorted trigonal-prismatic geometry. Tl–Tl distances in the sheet are 3.592, 3.679, and 4.057 Å. The Tl ions are arranged in zigzag chains in the metallic layers. The layers are completely separated by the benzotriazole anions, which are packed very closely together and are directed with all N atoms to the Tl layer. The structure of the layers is similar to that predicted for the protective layer formed when metal surfaces (i.e., copper) are treated with the corrosion inhibitor benzotriazole.

Introduction

It is well-known that the heterocyclic ligand benzotriazole (abbreviated BTAH) is a useful inhibitor for staining and tarnishing of many metals, and it is frequently used for corrosion inhibition on copper and its alloys.[2-4] Copper surfaces can be treated simply by immersion in a hot aqueous solution of BTAH or by treating with BTAH-impregnated wrapping paper.[2,5]

Although several investigations have been carried out on the nature of the protective layer,[2-6] the structure and even

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Table I. Final Positional[a] and Anisotropic[b] Thermal Parameters for (Benzotriazolato)thallium(I)

atom	x/a	y/b	z/c	U_{11} or U_{iso}[d]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Tl	0.53728 (1)	0.53314 (5)	0.62796 (1)	0.0410 (2)	0.0380 (2)	0.0291 (1)	0.0007 (1)	0.0044 (1)	−0.0012 (1)
N(1)	0.4208 (2)	0.077 (1)	0.5238 (4)	0.052 (3)	0.052 (3)	0.033 (3)	0.003 (3)	0.009 (2)	0.002 (2)
N(2)	0.4521 (2)	−0.066 (1)	0.6031 (4)	0.043 (3)	0.052 (3)	0.045 (3)	0.006 (3)	0.006 (2)	0.000 (2)
N(3)	0.4315 (2)	−0.065 (1)	0.7009 (3)	0.040 (3)	0.052 (3)	0.034 (3)	0.002 (3)	0.002 (2)	0.003 (2)
C(1)	0.3783 (2)	0.174 (1)	0.5748 (4)	0.034 (3)	0.031 (3)	0.027 (3)	−0.003 (3)	0.003 (2)	−0.003 (2)
C(2)	0.3342 (2)	0.334 (1)	0.5358 (4)	0.050 (4)	0.048 (4)	0.030 (3)	0.000 (3)	−0.008 (3)	0.002 (3)
C(3)	0.2991 (2)	0.404 (1)	0.6088 (4)	0.036 (4)	0.043 (4)	0.059 (4)	0.010 (3)	−0.005 (3)	−0.002 (3)
C(4)	0.3066 (2)	0.319 (1)	0.7200 (4)	0.035 (4)	0.045 (4)	0.044 (3)	−0.006 (3)	0.016 (3)	−0.006 (3)
C(5)	0.3488 (2)	0.158 (1)	0.7603 (4)	0.045 (4)	0.041 (3)	0.029 (3)	−0.009 (3)	0.006 (3)	−0.001 (3)
C(6)	0.3847 (2)	0.084 (1)	0.6862 (4)	0.037 (3)	0.031 (3)	0.029 (3)	−0.002 (3)	0.000 (2)	0.001 (2)
H(1)[c]	0.3299	0.3974	0.4577	0.04					
H(2)[c]	0.2679	0.5260	0.5808	0.04					
H(3)[c]	0.2799	0.3752	0.7719	0.04					
H(4)[c]	0.3538	0.0944	0.8361	0.04					

[a] The estimated standard deviations in the least significant figures are given in parentheses here and in other tables. [b] The thermal parameters are in the form $T = \exp[-2\pi^2 \Sigma_i \Sigma_j U_{ij} h_i h_j a_i^* a_j^*]$. [c] Parameters for hydrogen were not refined. [d] U_{iso} in Å^2.

the thickness of the layer are still subjects of considerable discussion.[6-8] Protection of metals with reactive materials capable of forming surface-phase coordination compounds is an area of chemistry which has a quite large technological impact. Chemical, physical and structural studies on realistic model compounds are needed to understand the very complex surface chemistry that leads to corrosion inhibition.

A search for crystalline Cu(I) and Cu(II) model compounds containing BTAH (or the anionic, deprotonated form BTA$^-$) has been unsuccessful so far. Nevertheless, comparison between reflection-UV and -IR spectra and ESCA data for the model compounds and the protective layer has indicated that a surface compound of approximate composition CuBTA, which is supposed to be very tight and close packed, may be present on the surface.[7,8] Because of the lack of crystalline Cu(I) benzotriazole compounds, we have examined other benzotriazole compounds which might indicate how BTAH interacts with metallic surfaces.

Thus far, only a few organometallic compounds of BTAH have been investigated by X-ray crystallography, namely, a trimeric[9] species $M_3(BTA)_6(allylamine)_3(Ph_3PO)_2$ containing N(1)–N(3) bidentate-bridging coordinated BTA and very recently $Ir(CO)(Ph_3P)_2(BTA)$ containing monodentate N(1) coordination.[10]

We now report the crystal and molecular structure of TlBTA, a compound having the same stoichiometry as the proposed surface compound CuBTA.

Experimental Part

Preparation of TlBTA. (Benzotriazolato)thallium was prepared from thallium(I) acetate and benzotriazole by using ethanol as the solvent and triethylamine as base. The procedure has been described elsewhere.[10] Slightly cream-colored blades were obtained after recrystallization from hot water. Crystal data for $C_6H_4N_3Tl$: formula weight 322.5; monoclinic, space group $C2/c$; $Z = 8$; $a = 26.605$ (3), $b = 4.057$ (1), $c = 12.173$ (2) Å; $\beta = 93.74$ (1)°; d(calcd) = 3.328 g/cm^{-3}; μ(Mo Kα) 246.8 cm^{-1}; $F(000) = 1136$ electrons; $V = 1311.2$ Å^3.

Accurate values of the unit cell parameters and the crystal orientation matrix were determined at ambient temperatures from a least-squares treatment of the angular settings of 20 reflections, carefully centered on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation (λ 0.71069 Å).[11] The unit cell parameters and systematic extinctions (hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$) allowed two space groups, Cc and $C2/c$. Structure determination excluded Cc. The standard deviations in the lattice parameters were derived from a comparison of the deviations from integer values of the indices, calculated with the orientational matrix, for the angular settings of the orientation reflections as described by Duisenberg.[12]

Collection and Reduction of the Intensity Data. The crystal used for data collection was a plate with dimensions 0.47 × 0.10 × 0.03 mm. Intensities for 3427 reflections up to $\theta = 27.5°$ were collected on the Enraf-Nonius CAD4 diffractometer, equipped with a scintillation counter and a graphite monochromator, in the ω-scan mode. The applied scan angle was $\Delta\omega = 1.30 + 0.35(\tan\theta)°$.

The background was measured in an additional scan area of $\Delta\omega/4°$ on both sides of the main scan with the same scan speed. The intensity of every reflection was measured at the highest possible speed and then, if needed, at a speed designed to achieve $I_{min} = 1000$ counts above background. The maximum time of measurements was $t_{max} = 120$ s. The horizontal and vertical detector apertures were 3 and 4 mm, respectively, and the distance between the crystal and the aperture was 173 mm.

The (020) reflection was used as a standard reflection, and its intensity was monitored every 0.5 h of X-ray exposure time. The net intensity was calculated with

$$I_{net} = (\text{scale})(S - 2(L + R))/\text{npi}$$

where $(L + R)$ is the total background count, S the scan count, and npi the ratio of the maximum possible scan speed to the applied scan speed. The data were scaled to compensate for short- and long-range fluctuations in the intensity.

The standard deviation in the net intensity was calculated with

$$\sigma(I) = (\text{scale}/\text{npi})(S + 4(L + R))^{1/2}$$

Correction for absorption was made by analytical integration with the crystal shape described by eight faces; factors ranged from 1.85 to 11.91. The intensities of 3247 reflections were averaged to give 1499 independent reflections of which 1297 have $I > 2.0\sigma(I)$; only these reflections were used in the structure determination.

The data were corrected for Lorentz and polarization factors (Lp). The $\sigma(I)$'s were converted to the estimated errors in the relative structure factors $\sigma(F)$ by $\sigma(F) = [(I + \sigma(I))/Lp]^{1/2} - (I/Lp)^{1/2}$.

Determination and Refinement of the Structure

The structure was solved by standard Patterson and Fourier techniques. Subsequent refinement of positional and anisotropic parameters by block-diagonal least-squares converged to $R_F = 0.024$. At this point, hydrogen positions were found in a difference Fourier map. Refinement of the nonhydrogen atom parameters was continued by full-matrix least-squares after the introduction of weights according to

$$w^{-1} = \sigma^2(F_o) + 0.0003F_o^2$$

The final R values for 1297 reflections are $R_F = 0.022$ and $R_{wF} = 0.024$.[13] A total of 91 parameters including one scale factor were varied. All shifts were less than half their standard deviations when the refinement was stopped. The positional and thermal parameters are presented in Table I. The average deviation in an observation of unit weight defined as

$$[\sum w(F_o - F_c)^2/(m - n)]^{1/2}$$

where m = number of reflections and n = number of parameters, was 3.09. A final electron density difference Fourier synthesis showed no significant residual electron density apart from some features less than 0.9 e Å^{-3} around the thallium atom (with a noise level of 0.4 e Å^{-3}).

Scattering factors for thallium, carbon, and nitrogen are those of Cromer and Mann.[14] The real part of the anomalous contribution

Table II. Bond Distances (Å) and Angles (deg) in TlBTA, As Well As Some Relevant Intermolecular Distances and Angles[a]

	Bond Distances		
Tl–N(1^{i})[b]	2.725 (5)	Tl–Tl$^{\mathrm{i}}$	3.592 (1)
Tl–N(2^{ii})	2.792 (5)	Tl–Tl$^{\mathrm{ii}}$	4.057 (1)
Tl–N(3^{iii})	2.732 (4)	C(2)–H(1)	0.98 (5)
Tl–N(1^{iv})	3.326 (5)	C(3)–H(2)	1.01 (5)
Tl–N(2)	3.323 (5)	C(4)–H(3)	1.01 (5)
Tl–N(3^{v})	3.271 (4)	C(5)–H(4)	0.96 (5)
Tl–Tl$^{\mathrm{v}}$	3.678 (1)		
	Bond Angles		
N(1^{i})–Tl–N(2^{ii})	87.3 (1)	N(2)–Tl–N(3^{v})	70.1 (1)
N(1^{i})–Tl–N(3^{iii})	93.1 (1)	N(1^{i})–Tl–N(1^{iv})	83.6 (1)
N(2^{ii})–Tl–N(3^{iii})	86.5 (1)	N(1^{i})–Tl–N(2)	132.0 (1)
N(1^{iv})–Tl–N(2)	69.9 (1)	N(3^{iii})–Tl–N(2)	132.6 (1)
N(1^{iv})–Tl–N(3^{v})	73.8 (1)	N(3^{iii})–Tl–N(3^{v})	84.5 (1)
	Intermolecular Distances		
N(1)–N(2^{iv})	3.810 (7)	H(1)–H(4^{vii})	2.64 (6)
N(1)–N(3^{vi})	3.961 (6)	H(1)–H(3^{vii})	2.71 (6)
N(2)–N(3^{v})	3.786 (6)	H(3)–H(2^{viii})	2.67 (6)
N(1)–C(5^{vi})	3.752 (7)	H(3)–H(3^{viii})	2.61 (6)
H(1)–H(4^{vi})	2.59 (6)		
	Intermolecular Angles		
N(1^{i})–Tl–N(3^{v})	139.8 (1)	N(2^{ii})–Tl–N(3^{v})	132.3 (1)
N(2^{ii})–Tl–N(1^{iv})	132.3 (1)	N(3^{iii})–Tl–N(1^{iv})	140.5 (1)
N(2^{ii})–Tl–N(2)	82.6 (1)		

[a] For distances and angles within BTA, see Table III. [b] Symmetry code: (i) $1-x$, $1-y$, $1-z$; (ii) x, $1+y$, z; (iii) $1-x$, $1+y$, $3/2-z$; (iv) $1-x$, $-y$, $1-z$; (v) $1-x$, y, $3/2-z$; (vi) x, $-y$, $-1/2+z$; (vii) x, $1-y$, $-1/2+z$; (viii) $1/2-x$, $-1/2+y$, $3/2-z$.

to the scattering factor for thallium was taken from ref 15. The values for H are those of Stewart, Davidson, and Simpson.[16] All computer calculations were performed on a CDC CYBER-73 computer at the computer center of the University of Utrecht. Programs used in this structure analysis included the programs CAD4TAPE (for handling the diffractometer output by D. Kaas), ORTEP (thermal ellipsoid drawings by Johnson[17]), and an extended version of the XRAY-76 system (by Stewart[18] and implemented by the Dutch XRAY system group) for most of the other calculations.

Results and Discussion

Description of the Structure. The crystal structure of TlBTA can best be considered as a layer structure in which Tl(I) ions comprise a zigzag layer with BTA$^-$ ligands coordinated above and below the layers, thereby separating the layers from each other. A projection of the structure along the *b* axis is shown in Figure 1. This figure also shows the geometry of the BTA ligands and the projection of the Tl–N bonds. The coordination polyhedron around Tl is shown separately in Figure 2.

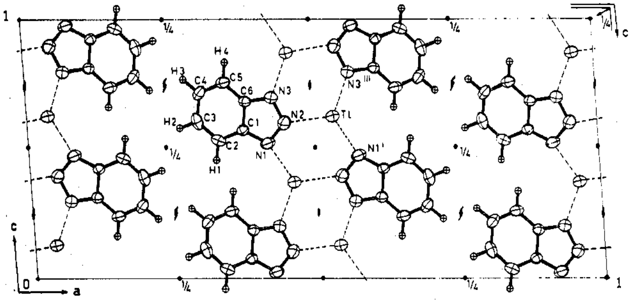

Figure 1. Projection of the structure down the *b* axis. The numbering scheme and short Tl–N distances are indicated. The ellipsoids are drawn at the 50% probability level. Hydrogens are represented as artificially drawn spheres.

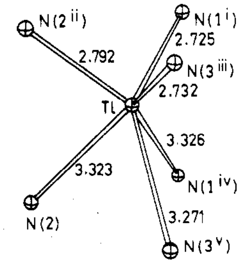

Figure 2. Coordination geometry around Tl in TlBTA; see Table II for symmetry code.

The coordination geometry around Tl can best be described as distorted trigonal prismatic. The distortion is demonstrated by the asymmetric location of Tl(I) in the polyhedron. The height of the prism amounts to 4.057 Å (*b* axis), whereas the sizes of the trigonal planes are 3.786 × 3.810 × 3.961 Å.

Bond distances and angles are listed in Table II, except for the distances and angles concerning the carbon and nitrogen atoms of BTA; these are listed in Table III, together with the other data[9,10,19] for BTA compounds.

As seen from Table III, all bond lengths and angles are very close to those of the other BTA compounds. This means that only small differences occur between coordination as a monodentate ligand (to Ir and to H$^+$), as a bidentate chelating ligand (to pairs of Ni(II)), and as a tridentate chelating ligand (to Tl(I) ions).

Table III. Bond Lengths (Å) and Angles (deg) in TlBTA and Some Other BTA Compounds

distance or angle	tridentate TlBTA	bidentate (N(1), N(2))[a] $Ni_3(BTA)_6(AA)_6$	monodentate (N(1))[b] $IrCO(Ph_3P)_2BTA$	acid (N(1))[c] BTAH
N(1)–N(2)	1.362 (6)	1.333 (7)	1.344 (6)	1.346 (10)
N(2)–N(3)	1.342 (6)	1.328 (7)	1.335 (6)	1.310 (7)
N(3)–C(6)	1.385 (7)	1.339 (8)	1.358 (7)	1.362 (35)
C(6)–C(1)	1.403 (7)	1.396 (9)	1.383 (7)	1.389 (10)
C(1)–N(1)	1.381 (7)	1.385 (8)	1.366 (6)	1.366 (11)
C(6)–C(5)	1.389 (8)	1.437 (9)	1.416 (8)	1.409 (9)
C(5)–C(4)	1.362 (8)	1.399 (12)	1.376 (9)	1.368 (10)
C(4)–C(3)	1.399 (7)	1.417 (12)	1.387 (9)	1.405 (10)
C(3)–C(2)	1.361 (8)	1.386 (12)	1.370 (8)	1.367 (5)
C(2)–C(1)	1.398 (8)	1.431 (10)	1.398 (7)	1.404 (8)
C(1)–N(1)–N(2)	106.4 (4)	105.5 (5)	107.8 (4)	110.3
N(1)–N(2)–N(3)	111.2 (5)	112.7 (5)	110.4 (4)	108.8 (8)
N(2)–N(3)–C(6)	107.5 (4)	106.7 (5)	106.8 (4)	108.2 (4)
N(3)–C(6)–C(1)	106.8 (4)	108.5 (5)	108.8 (5)	108.4 (3)
C(6)–C(1)–N(1)	108.0 (4)	106.5 (5)	106.1 (4)	104.2 (8)
C(6)–C(5)–C(4)	117.1 (5)	116.6 (7)	116.9 (6)	116.2 (7)
C(5)–C(4)–C(3)	121.9 (5)	120.3 (6)	122.0 (6)	122.2 (4)
C(4)–C(3)–C(2)	121.4 (5)	124.6 (8)	121.9 (7)	122.7 (1)
C(3)–C(2)–C(1)	118.2 (5)	114.5 (7)	116.8 (6)	115.3 (5)
C(2)–C(1)–C(6)	119.7 (5)	122.5 (5)	122.3 (5)	122.7 (7)
C(1)–C(6)–C(5)	121.8 (5)	121.1 (6)	120.1 (5)	121.5 (5)

[a] See ref 9. [b] See ref 10. [c] See ref 19.

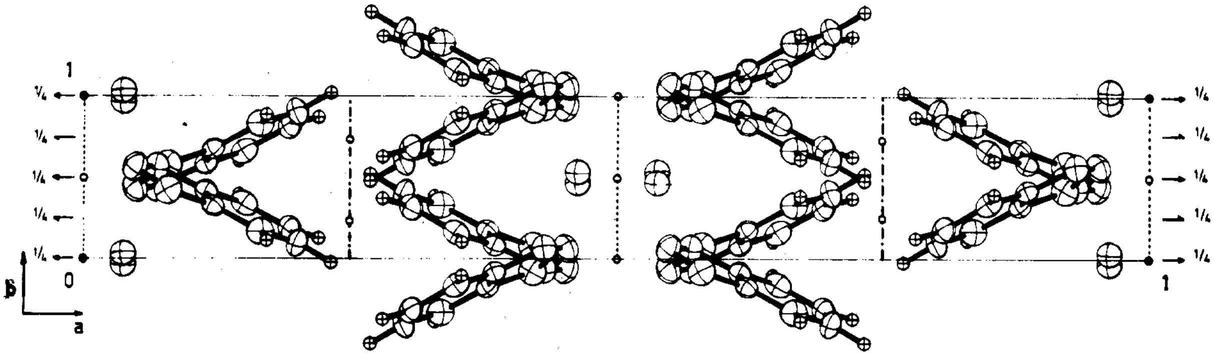

Figure 3. View of TlBTA as seen along the crystallographic *c* axis.

Table IV. Least-Squares Plane through Benzotriazole and the Distances of the Thallium Atoms to That Plane[a]

Deviations, Å			
N(1)	0.009	C(3)	0.004
N(2)	0.016	C(4)	0.018
N(3)	−0.004	C(5)	−0.001
C(1)	−0.010	C(6)	−0.022
C(2)	−0.011		

Distances, Å			
Tl(x, y, z)	3.170	Tl($1-x, -y, 1-z$)	−2.036
Tl($x, y-1, z$)	−0.418	Tl($1-x, y, {}^3/_2-z$)	2.859
Tl($1-x, 1-y, 1-z$)	1.552	Tl($1-x, y-1, {}^3/_2-z$)	−0.731

[a] Equation of the plane (the planes are defined in fractional coordinates): $11.179x + 3.588y + 2.136z = 6.091$.

The geometry around Tl needs some further comments. In more or less ionic Tl(I) compounds,[20,23] structures with either three, four, or five relatively short Tl–L bonds have been found, usually with two or three additional longer Tl–L bonds. The present structure has the Tl ion coordinated by three nitrogen atoms at an average distance of 2.750 Å, with average N–Tl–N angles of 89.0°. The other nitrogen atoms are at an average of 3.307 Å with N–Tl–N angles (averaged) of 71.3°. The bond angles N(short)–Tl–N(long) in the trigonal prism average 83.6 and 134.9°.

Although it is clear that the three long Tl–N distances are within the coordination sphere around Tl, it should be mentioned that several Tl–N and Tl–C distances occur in the 3.42–3.95-Å region. These distances, however, are in fact "behind" the bonding atoms and cannot be considered associated with coordination.

The fact that Tl(I) is not at the center of the trigonal prism might be due to the stereochemically active lone pair of electrons which can be thought to be directed in the pseudotrigonal direction. Similar structural evidence[20,23] has been reported for Tl_2MO_3 (M = Ti, Sn) and Tl_2CO_3. In these compounds either three, four, or five ligands are bonded at a short distance on *one* side of the metal, whereas much longer distances are found in the *other* direction.

The benzotriazolato ligands are almost planar as seen from Table IV. The Tl atoms are alternatively above and below these planes. The packing of TlBTA in the crystal is shown in Figure 1. A projection along the *c* axis is shown in Figure 3. The complete separation of the layers by the BTA ligands is indeed evident.

The Tl–Tl distances in the layer, however, are not unusually small (3.592, 3.678, and 4.057 Å) and are larger than those observed in, e.g., Tl_2SnO_3 (3.23 Å),[23] Tl_5Te_3 (3.32 Å and above),[22] Na_2Tl (3.224 Å),[23] and metallic thallium (3.4007 Å).[21] The Tl–Tl distances in Tl_2CO_3 (3.588, 3.693, and 3.777 Å) and Tl_2SO_3 (3.846–4.000 Å) on the other hand are comparable[20,24] to our results, although the coordination polyhedra are completely different. The Tl–Tl distance and orientation in our compound is clearly influenced by the geometry of the ligand; the location of the Tl ions in the layer is mainly determined by the BTA anion sticking into the layer.

Possible Relationship with Mechanism of Corrosion Inhibition. As said in the Introduction, benzotriazole is an important corrosion inhibitor, and many studies have been undertaken with respect to the interaction of BTA and derivatives with copper compounds and copper surfaces. Apparently a very tight, close-packed, inert layer of some surface compound is responsible for this protective action.

Recent results[7,8,25] applying ESCA and microspectrofluorimetry indicate that cuprous benzotriazole forms when copper metal is treated with BTAH. Arrow-like, tridentate coordination of benzotriazole has not been previously reported but may provide a model for the interaction of this ligand with a copper surface. Although the ionic and metallic radii of Tl and Cu are different (e.g., the ionic radii are reported[26] to be ~1.0 and 1.50 Å for hexacoordinate Cu(I) and Tl(I), respectively), a similar surface structure in the case of BTA-treated copper might well be possible. Due to the smaller radius, the structure might even be tighter and more closely packed, with BTA molecules sticking into the Cu surface. Although such a structure with firmly packed BTA in the surface can contribute to its inertness, other factors, such as cross-linking by partial oxidation to Cu(II), almost certainly yield additional stabilization. Nevertheless, in TlBTA the contacts between benzotriazole rings are very close with almost no open spacings. In the direction of the *b* axis, the shortest C–C, N–N, and C–N distances are 3.62–3.68 Å. In the *a–c* plane the closest contacts are H(3)···H(3′) = 2.61 Å and C(4)···C(4′) = 3.74 Å in the direction of *a*. In the direction of *c* the closest distances are H(1)···H(4) = 2.59 Å, C(2)···C(5) = 3.95 Å, and N(1)···C(5) = 3.75 Å. These latter distances might even be shorter in the case of copper, owing to its smaller radius. Unfortunately, no suitable single crystals of CuBTA have been obtained so far. Nevertheless, we now have evidence that BTA is able to coordinate as a tridentate ligand bridging between several metal ions. Moreover, we have shown that the BTA ligands, while coordinated to the metal surface can be arranged in such a way that the surface is almost completely covered.

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Supplementary Material Available: A listing of structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of 1,5′-Bidecaboran(14)yl: A New Borane from γ Irradiation of Decaborane(14)[1]

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The previously unknown structure of the most abundant of several isomers $B_{20}H_{26}$ produced by γ irradiation of decaborane(14) has been determined by X-ray crystal-structure analysis. The molecule, named 1,5′-bidecaboran(14)yl, is made up of a 1-decaboran(14)yl group linked by a two-center B–B bond to a 5-decaboran(14)yl group. The linking B1–B′5 bond, a type for which no previous precise metrical data exist, has a length of 1.698 (3) Å. The interatomic distances and angles in the decaboranyl groups, after correction for the effects of thermal motion, agree remarkably well with the corresponding ones in decaborane(14) known from analysis of low-temperature neutron-diffraction data. Most of the larger differences are for distances and angles involving atoms B1 and B′5 of the connecting link. Crystallographic data: monoclinic, space group $P2_1/n$, $a = 7.235$ (1) Å, $b = 15.453$ (4) Å, $c = 14.895$ (3) Å, $\beta = 91.42$ (2)°, 4 formula units per cell, $d_{\text{calcd}} = 0.967$ g/cm^3 [λ(Cu Kα) 1.5418 Å].

The preparation by γ irradiation of decaborane(14) and the partial characterization of eight isomeric boranes of empirical formula $B_{20}H_{26}$ are described elsewhere by Pinson, Ingram, and Brown.[3] Each of the isomers was presumed to be made up of two of the various moieties $B_{10}H_{13}$ theoretically producible by abstraction of a single hydrogen atom from the decaborane(14) molecule. The isomer whose structure is described here is the most abundant one, accounting for 70% of the total irradiation product. Its infrared spectrum suggested molecular asymmetry. It was the only one for which crystals had been grown at the time the X-ray work was started.

Experimental Section

Unit Cell and Space Group. Only two single crystals large enough to be used were available. These were colorless, cloudy crystals of rather poor quality, grown by evaporation of solvent from a solution of the compound in cyclohexane. The smaller of the two crystals was used to make precession photographs, from which the space group was established as $P2_1/n$[4] (systematic absences: $h0l$ for $h + l$ odd and $0k0$ for k odd) and approximate cell parameters were obtained. Precise values for the cell parameters were derived by the method of least squares[5] from angle data for reflections from the second crystal recorded at 21–22 °C with the Oak Ridge computer-controlled diffractometer.[6] Data for 28 reflections in the range 11–85° in 2θ for Cu Kα radiation (unresolved doublet, λ 1.5418 Å) yielded the following parameters (and standard errors in parentheses): $a = 7.235$ (1) Å, $b = 15.453$ (4) Å, $c = 14.895$ (3) Å, $\beta = 91.42$ (2)°. The reasonable density 0.967 g/cm^3 was calculated on the assumption of four $B_{20}H_{26}$ formula units per cell.

Reflection Data. The crystal used in collecting the intensity data was the second and larger of the two available. With dimensions about 0.15 × 0.35 × 0.7 mm, it was somewhat longer than optimum for the 0.5-mm aperture of the collimator, but we were afraid to attempt to trim it for fear of losing it. We also needed all the intensity we could get, even at the risk of having slightly less accurate measurements.

The crystal was far from an ideal specimen. The effective mosaic spreads were about 2.7° and 1.7° (full width at background, allowing for partial splitting) for reflection vectors approximately perpendicular and parallel, respectively, to the ϕ axis, which was ~3° from the **a***direction. To achieve proper integration of the reflection intensities, it was necessary to use the triple ω-scan technique[7] as was used with a hexachlorobenzene crystal[8] of similar mosaicity. In this somewhat unusual procedure the height (dimension parallel to the 2θ axis) of the receiving aperture was set at the maximum, corresponding to an acceptance angle of 1.8°, and the width of the aperture was set by calculation as described by Einstein[7] to angles from 0.9 to 1.8° depending upon the particular 2θ range being recorded. The takeoff angle was 1.5°. The ω-scan range was 3.5°, and the step width was 0.05°. The counting time was 4 s at each point in the main scan and 2 s at each point in each background scan. The radiation was Cu Kα, unfiltered below 45° in 2θ and filtered through nickel foil above 45°. It was shown by varying the slit widths for selected reflections that no significant intensity was being excluded by the slits.

Over a period of about 6 weeks, 2953 intensities, representing 2663 independent reflections, were recorded at 21–22 °C with the automatic diffractometer to the limit 125° in 2θ. Data recorded regularly every 50 observations for three reference reflections showed an average 2% decline of intensity over the course of the data taking, indicating slight deterioration from effects of the X radiation or from contact with the air. From the raw intensity data and corresponding standard errors, the structure-factor squares, F_o^2, were calculated in the usual preliminary data processing,[9] along with standard errors, $\sigma(F_o^2)$, with corrections for the deterioration and for absorption and with averaging of the small number of replicate and equivalent reflections. The value of the absorption coefficient used was 1.89 cm^{-1}; the absorption

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